UNIVERSITY OF FLORIDA
GAINESVILLE, FLORIDA 32603

QUANTUM THEORY PROJECT
NUCLEAR SCIENCES BUILDING

June 24, 1966

Re: Semi-Annual Status
Report, NASA Re-
search Grant
NsG-512

Dr. T. L. K. Smull, Director
Office of Grants and Research Contracts
Attention: Code SC
National Aeronautics and Space Administration
Washington, D.C.

Dear Dr. Smull:

With this letter I would like to submit the fifth

Semi-Annual Status Report for the NASA Research Grant NsG-512

to the University of Florida concerning the subject:

Quantum Theory Studies of the Energies

of Excited State Atoms and Molecules,

Particularly as They Occur in the

Upper and Stellar Atmospheres, and in

Materials Undergoing Combustion.

We would like to express our sincere gratitude to

the National Aeronautics and Space Administration for making

this work possible.

Yours sincerely,

Darwin W. Smith
Assistant Director
Quantum Theory Project

DWS:jd

Enclosures   for Per-Olov Löwdin

cc: V. R. Learned
        P. O. Löwdin
        S. S. Ballard
        H. H. Sisler

March 31, 1966

For the period October 1, 1965
to March 31, 1966; NASA Research
Grant NsG-512 to the University
of Florida for basic scientific
research on the subject:

"Quantum Theory Studies of the
Energies of Excited State Atoms
and Molecules, Particularly as
They Occur in the Upper and Stellar
Atmospheres, and in Materials
Undergoing Combustion".

List of Papers Accompanying This Status Report

Technical Report No.	Author	Title	No. of Copies
66	G. Ludwig Hofacker	Theory of Internal Relaxation in Chemical Kinetics	5
76	J. O. Hirschfelder	Determination of Intermolecular Forces	5
Special Issue	P. O. Löwdin	The Calculation of Upper and Lower Bounds	5

Outline of Research in Progress

We have continued to devote much of our attention to the theory of
quantum mechanical lower bound procedures, and applications to two-electron systems.
The present status of the lower bound work using the partitioning technique is re-
viewed in a special report, "The Calculation of Upper and Lower Bounds of Energy
Eigenvalues in Perturbation Theory by Means of Partitioning Technique," by Professor
P. O. Löwdin. It is shown that, if $\mathcal{E}$ is a real variable, one may construct a
single- or multi-valued function $\mathcal{E}_1 = f(\mathcal{E})$ such that each pair $\mathcal{E}$ and $\mathcal{E}_1$
bracket at least one true eigenvalue E. If $\mathcal{E}$ is chosen as an upper bound by means
of the variation principle, the function $\mathcal{E}_1$ is hence going to provide a lower
bound. The partitioning technique is here used to derive Brillouin-type and
Schrödinger-type perturbation expansions and, in the case of a positive definite
perturbation $V > 0$, upper and lower bounds for the sums are determined by means of
operator inequalities. By using the method of "inner projection", it is further
shown that the remainders in the Brillouin-type expansion may be evaluated with any
accuracy desired, and the corresponding problem for the Schrödinger-type expansion
is briefly discussed.

Dr. J. H. Choi, who completed a doctoral dissertation entitled "Lower
Bounds to Energy Eigenvalues by the Partitioning Technique" last year, has remained
with the Quantum Theory Project through June 1966. Two papers have been prepared
based on his dissertation and the further work he has done this past year. (Pre-

prints will be sent when available). In the first paper (written in collaboration with D.W. Smith), "A Lower Bound Procedure for Energy Eigenvalues by the Partitioning Process," a method is described for treating the difficult case where the upper bound is greater than the first excited eigenvalue of $\mathcal{H}_o$. This method consists in the use of a multi-dimensional reference manifold which includes all of the eigenfunctions of the unperturbed Hamiltonian, the eigenvalues of which are less than or equal to the upper bound of interest. Applications to the two-electron iso-electron ions are given.

In Dr. Choi's second paper, "Treatment of Degeneracies in the Schrödinger Perturbation Theory by Partitioning Technique," the degenerate case is treated by two methods. The first uses a multi-dimensional reference manifold; the other uses "repeated partitioning" which enables one to use a one-dimensional reference space. While Löwdin had previously treated degeneracies in $\mathcal{H}$ itself, the present work was directed toward relating the Schrödinger Perturbation formula with the partitioning technique for a degenerate level of $\mathcal{H}^o$. Generalized wave and reaction operators W and t are introduced in connection with the repeated partitioning. The use of W and t in handling the degenerate case of $\mathcal{H}^o$ is discussed.

Further refinements in the method for obtaining lower bounds have been developed by Mr. Timothy Wilson in his doctoral dissertation which is nearing completion. He is studying the excited singlet states of the helium atom (2^3S and 3^3S) and the lithium ion (2^3S, 3^3S, and 4^3S). Upper and lower bounds agree to 0.00004 a.u. for the lowest singlets of each of these species, which is excellent agreement. For the other states, the agreement is less close, but still satisfactory.

A third doctoral dissertain was completed recently--that of Dr. Oswaldo Goscinski. He has surveyed the present status of the partitioning technique and lower bound theory, including its relation to the Temple formula, the Feenberg perturbation series, and the method of reciprocal variational problems. Dr. Goscinski also discussed a transformation of the Schrödinger equation which always yields a positive Hermitian operator, and this may clarify one of the problems in extending the theory to molecules.

The integrals necessary to apply these methods in the atomic case have been evaluated in closed form and applications are forthcoming.

There is a symmetry dilemma in the ordinary Hartree-Fock schemes based on Slater determinant. Dr. Löwdin has shown that the symmetry requirements aint which raises the energy, and that any lowering of the energy is

possible only at the expense of loss of symmetry. In the projected Hartree-Fock scheme, the total wave function is approximated by a specific projection $\mathcal{O}D$ in the component analysis of D, to which the variation principle is then applied. It is shown that the resulting wave function is directly connected with the independent-particle model in the sense that it is uniquely determined by a set of N spin-orbitals, where N is the number of particles. The properties of this scheme are discussed in some detail, and references to applications are given in a manuscript which is under preparation.

Mr. Carlos Bunge has been carrying out some atomic calculations by the method of configuration interaction. The preliminary results obtained for the ^{1}S states of Be are encouraging and we believe that we shall be able to obtain significantly better energies and wave functions than those found previously by other authors. The new techniques employed include:

a) a complete automatic program to handle the generation of a many-electron Hamiltonian matrix of a dimension limited only by time considerations.

b) a program to improve approximate eigenvalues and eigenvectors of large finite Hermitian matrices by the method of Gauss - Seidel - Lanczos.

c) the idea of finding the natural orbitals of the K and L shells, to select some, and to construct from them a new basis of one-electron functions. This is shown to improve considerably the basis set used by Watson (Phys. Rev. $\underline{109}$, 170 (1960)). As an illustration, we are getting for the Be ground state with a basis of 4 s-type and 3 p-type orbitals the same results as Weiss (Phys. Rev. $\underline{122}$, 1826 (1961)) with 7 s and 5 p orbitals. Also our basis is orthogonal, which means that we can extend our calculations almost without restrictions.

Dr. Rolf Manne has developed an approximate molecular orbital LCAO-SCF scheme with the aim of calculating shifts of inner electron levels due to chemical bonding. Analytical atomic Hartree-Fock functions are used as a basis, and the matrix elements are written in a form lending itself to the introduction of calculated or experimental atomic orbital energies. The latter case is equal to the Goeppert-Mayer-Sklar approximation in π --electron theory. The outer or valence electrons and the inner or core electrons are treated separately, and the core-valence interaction can be included rigorously by means of Löwdin's partitioning technique leading to expressions which in the first approximation are equivalent to those occurring in the psendopotential interpretation of the OPW method by Phillips and Kleinman. Preliminary semiempirical calculations have been performed for SO_4^{2-}, SO_3^{2-}, and $S_2O_3^{2-}$, giving reasonable agreement with measured shifts in the X-ray emission spectra.

Dr. C. E. Reid is developing a computer program for calculating integrals needed in finding lower bounds for the H_2 molecule. He is also studying alternatives to the usual power series expansions for perturbations, especially for those occuring in the united-atom expansion and the oscillator with a forth-power perturbation, where the expansions either do not exist or have only asymptotic valid validity. For the oscillator with a term in X^4, a convergent continued fraction was found for expressing the energy.

In order to evaluate the performance of different approximate methods, a full configuration interaction treatment was carried out by Dr. Ruben Pauncz for the ground state of fulvene. The number of configurations used is 95. These results served as reference points for judging the performance of different methods. The following approximate treatments were tested:

a) AMO method with one parameter

b) AMO method with five parameters

c) AMO method with the best MO's

d) Linear combination of AMO wave functions, using different spin coupling schemes.

The results show that it is not worth while to include the linear combination of different spin coupling schemes; it does not lead to appreciable improvement. On the other hand, it is important to determine the best molecular orbitals used in the construction of the AMO wave function.

An alternative treatment which also uses the idea of different orbitals for different spins (non-paired spatial orbital method-Linnett) was tried also. The wave function was decomposed into configurational functions. The best function, using only one non-linear parameter, gave a result which was the closest one among all the methods investigated. A further improvement was obtained by the use of different spin coupling schemes.

The NPSO method comes very close to the result of the full configuration interaction treatment; it gives more than 90 per cent of the energy improvement. The AMO's method yields only 60 per cent. The latter method has more potentialities for treatment of large systems.

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